(12) UK Patent Application (19) GB (11) 2 190 100 (13) A

(43) Application published 11 Nov 1987

D1

(21) Application No 8710852

(22) Date of filing 7 May 1987

(30) Priority data

(31) 3615425 (32) 7 May 1986 (33) DE

(71) Applicant
Thyssen Edelstahlwerke AG,

(Incorporated in FR Germany),

Postfach 730, 4150 Krefeld 1, Federal Republic of Germany

(72) Inventors
Hanns-Gert Bitter Dr Ing,
Klaus Rudinger Dr Ing

(74) Agent and/or Address for Service
Hyde Heide & O'Donnell, 146 Buckingham Palace Road, London SW1W 9TR

(51) INT CL[4]
C22C 14/00

(52) Domestic classification (Edition I)
C7A 747 765 A231 A233 A235 A237 A239 A23Y A241 A249 A24X A250 A253 A255 A257 A259 A25Y A260 A263 A266 A269 A279 A280 A289 A28Y A290 A299 A300 A303 A305 A307 A309 A30Y A311 A313 A31X A329 A330 A339 A33Y A349 A34Y A350 A352 A354 A356 A358 A35Y A360 A362 A369 A36Y A370 A37X A37Y A390 A394 A396 A398 A39Y A409 A410 A414 A416 A418 A41Y A422 A425 A428 A42X A439 A440 A44Y A481 A483 A485 A487 A489 A48X A48Y A491 A49X A509 A514 A51X A51Y A529 A53X A53Y A549 A551 A553 A555 A557 A559 A55X A55Y A56X A579 A584 A58X A58Y A599 A609 A61X A61Y A629 A671 A672 A673 A675 A677 A679 A67X A67Y A681 A682 A683 A685 A686 A687 A688 A689 A68X A68Y A693 A694 A695 A697 A699 A69X A70X
C7U 9A
U1S 1637 1783 1901 1987 1990 2016 2026 2032 2034 2037 2038 C7A C7U

(56) Documents cited
GB 1389562
Metals and Materials Vol 1 No 12 (Dec 1985) pp 739-44

(58) Field of search
C7A
C7U
Selected US specifications from IPC sub-classes C22F C22C

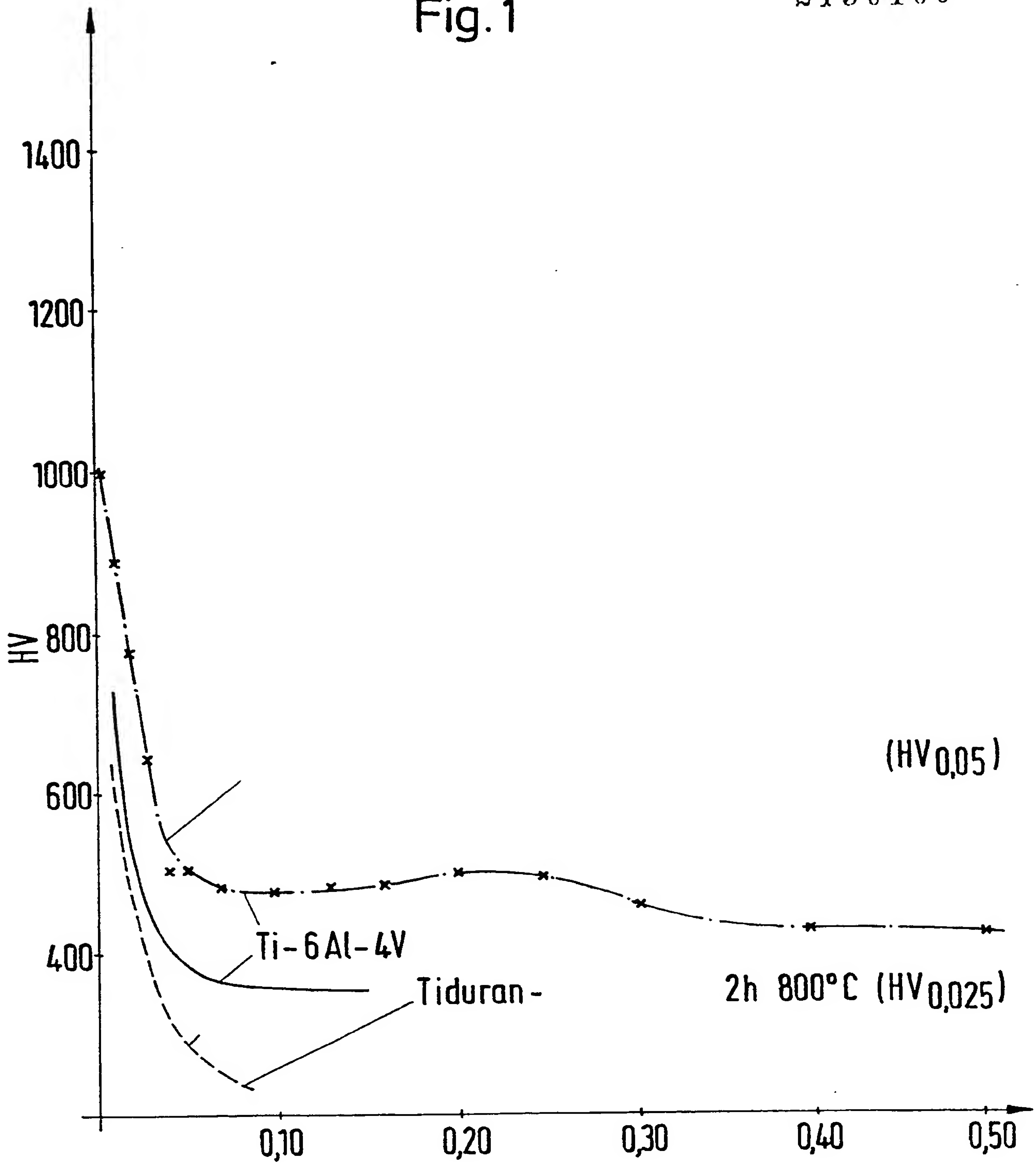
(54) A titanium alloy and machine parts made therefrom

(57) A titanium alloy forged, cast or sintered to form a machine part has a tensile strength of at least 640 N/mm^2. The alloy contains between 3 and 28% of one or more of the elements aluminium, chromium, iron, hafnium, cobalt, copper, manganese, molybdenum, nickel, niobium, palladium, silver, silicon, tantalum, vanadium, tungsten, tin, zirconium, beryllium, boron, carbon, oxygen, rare earths and yttrium, the remainder titanium together with unavoidable impurities. The surface layers of the alloy part are treated at over 700°C in glow-discharge plasma, in order to improve resistance to abrasion, including erosion and cavitation and/or in order to increase the permissible surface pressure, the treatment gas containing small quantities (partial pressures 0.1 to 500 mbar) of nitrogen.

GB 2 190 100 A

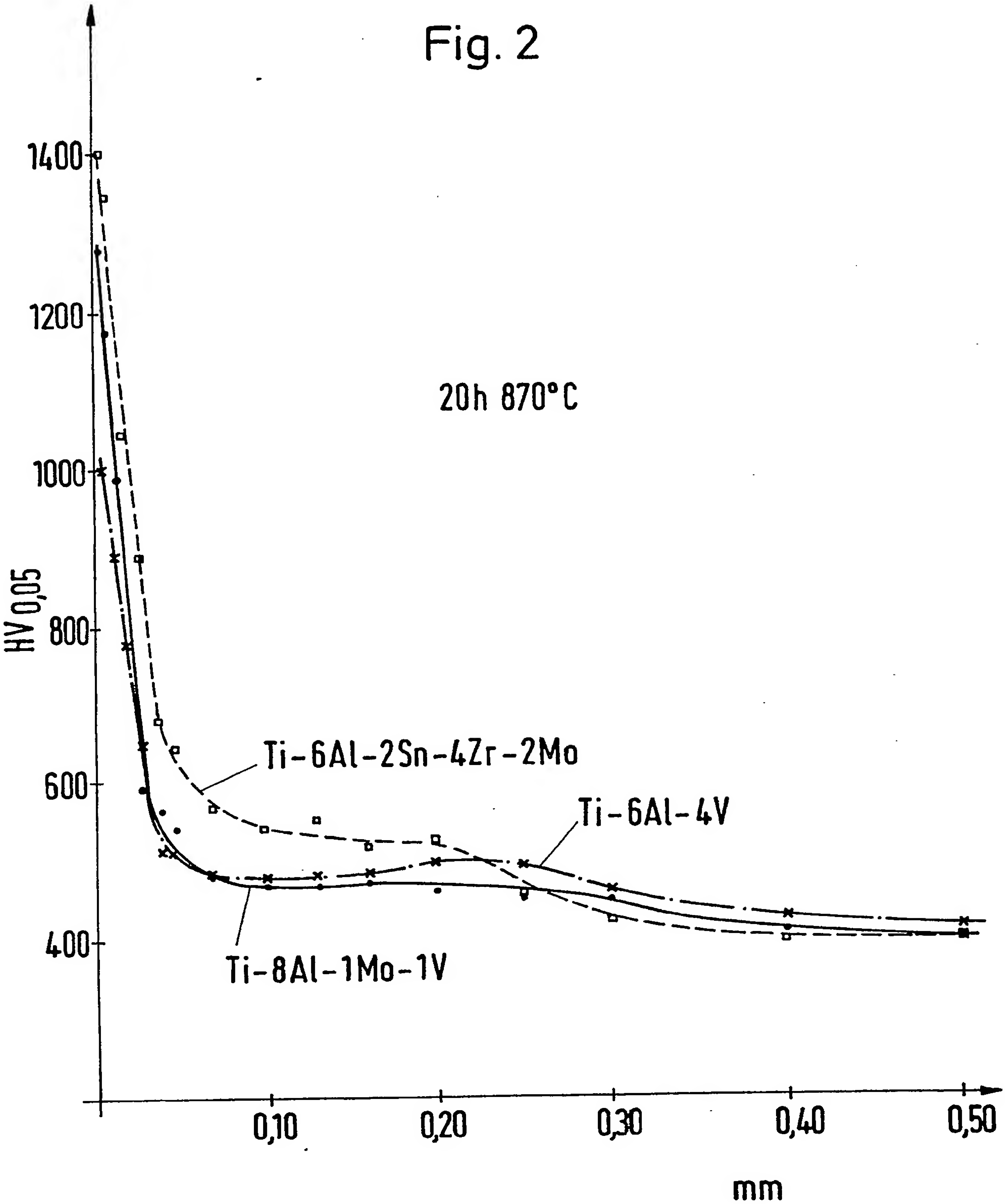
2190100

Fig. 1



2190100

Fig. 2



SPECIFICATION

A titanium alloy and machine parts made therefrom

The invention relates to a forged, cast or sintered technical titanium alloy and to machine parts made therefrom, the alloy being of either α, or $\alpha + \beta$. or β type and being for use in machine parts whose surface layers are treated at above 700°C in glow-discharge plasma for improving abrasion resistance, including resistance against erosion and cavitation and/or in order to increase the permissible surface pressure; and in which the elements necessary for forming the surface layers are derived from a treatment gas containing small quantities (partial pressure 0.1 to 0.4 mbar) of nitrogen and, if necessary, carbon and/or oxygen.

Machine parts are nowadays usually made from steels of certain composition groups. Particularly interesting for high-value parts in stationary motors and turbines and in motors and transmissions for motor vehicles and aircraft and, in general, for machine parts which reciprocate rapidly, are titanium alloys, due to their high strength-to-density ratios. Nevertheless, quite apart from the cost of these alloys, their poor wear-resistance has hitherto prevented them from enjoying a wide use.

Many methods have been proposed for remedying the tendancy of parts made from titanium and titanium alloys to weld together where they slide in contact with each other, by giving the parts abrasion-resistant coatings. But all the hitherto known methods have disadvantages. Galvanic coatings do not adhere well. Sprayed-on anti-abrasion layers have limited uses due to the inhomogeneous transition at the phase-boundary surface of the substrate material. This also applies to the titanium nitride layers of micrometre thicknesses applied by the PVD and CVD processes.

In the salt bath, or in the gas phase, it is possible by diffusing elements low on the Periodic Table into the surface of a part made of titanium or a titanium alloy to form zones of mixed crystals containing continuously changing concentrations of foreign atoms. But in large-scale manufacture, for various reasons, the diffusion zones, and the resulting hard layers, are limited in depth to only, for example, 0.03 to 0.06 mm.

This also applies to gas nitriding in nitrogen or ammonia, and to carburising in pure wood charcoal. Even the Tiduran process, which is the most used in industrial practice, gives only the hardness depths shown in Figure 1.

The intention in the present invention is to provide a titanium alloy for machine parts which is capable of acquiring a diffusion zone with a greater hardness depth than has hitherto been attainable.

To solve this problem it is proposed, according to the invention, to use in machine parts a technical titanium alloy with a tensile strength of at least 640 N/mm^2 and the alloy containing between 3 and 28% of one or more of the elements aluminium, chromium, iron, hafnium, cobalt, copper, manganese, molybdenum, nickel, niobium, palladium, silver, silicon, tantalum, vanadium, tungsten, tin, zirconium, beryllium, boron, carbon, oxygen, rare earths and yttrium, the remainder titanium together with unavoidable impurities; such an alloy being used for making machine parts whose surface layers are treated at over 700°C in glow-discharge plasma, in order to improve resistance to abrasion, including erosion and cavitation and/or in order to increase the permissible surface pressure, the treatment gas containing small quantities (partial pressures 0.1 to 500 mbar) of nitrogen.

Preferably the surface treatment includes the use of a gas which can contain, besides nitrogen, also small quantities of carbon and/or oxygen, for the purpose described above.

The treatment time should be at least one hour and the hardened depth at leat 0.02 mm, preferably 0.25 mm.

The α-fraction, particularly in ($\alpha + \beta$)- alloys, is advantageously being diminished by solution heat treatment.

Preferably also, the glow-discharge plasma treatment takes place at a temperature which, in order to increase diffusion velocity, is not more than 200°C under the β-transition temperature for the alloy.

In the titanium alloy as claimed herein, the internal stresses resulting from preliminary treatments, or the structural changes associated with volume changes, can be largely nuetralised at the treatment temperature by a low-stress annealing of the pre-worked parts, the temperature of the stress-relief annealing being of the same order, if necessary up to 50°C higher, than the subsequent treatment temperature.

The machine parts being in a practically finished state before treatment be glow-discharge plasma, any subsequent machining, such as polishing, honing or lapping, for correcting small increases in volume or roughness, is advantageously controlled to take less than 0.020 mm of surface away.

The alloy now provided may be used for spindles, transmission shafts, toothed wheels, toothed rods, rolls, rollers, pinions, synchronisation rings, chain links, plain, ball, roller and needle bearings, crankshafts and camshafts, connecting rods, piston rings, valve rockers, valves, the leading edges of steam turbine blades, conveyor worms, cylinders, nozzles, sonotrodes and the cutting edges of parting tools.

The hardness at distances of 0.05 and 0.1 mm from the surface, i.e. the 0.05 and 0.1 mm hardnesses, and the depths from the surface at which hardness values of at least 600 HV can still be detected, are distinctly improved, in the titanium alloy of the present invention, after the parts have been given the specified surface treatment in the plasma of a glow discharge. Whereas in the Tiduran-treated alloy the 0.05 hardness is approximately the core hardness, i.e. practically no hardening has taken place, the plasma-treated sample shows an 0.05 hardness of 500 HV. The hardened depth of this sample is therefore about three times greater than it is after the Tiduran treatment.

Figure 1 demonstrates this improvement.

A further process advantage is that the greater hardened depth obtainable in principle by the plasma treatment can in practice be fully utilised because, in contrast to the surfaces attacked in the salt bath, the plasma-treated surfaces require little or no subsequent finishing. This makes it possible to utilise fully the different properties of the three layers which are typical of titanium alloys.

The micrographs of three titanium alloys of this invention, treated in a glow-discharge plasma, whose hardness curves are shown in Figure 2, all show the same compound-layered structure.

The outermost layer is a titanium nitride layer 1 to 2 micrometres thick and of greater density. This layer has a yellowish appearance in the metallographic polished specimen. Under that there is a white #-stabilised layer about 5 micrometres thick, which merges into the 0.15 to 0.40 mm diffusion layer showing inwards-decreasing concentrations of interstitial elements (nitrogen, carbon, oxygen).

Figure 2 shows clearly the advantages of treating titanium alloys in glow-discharge plasma, compared with other diffusion methods in the gas phase, in the salt bath or working with powders, these advantages resulting from the greater number of adjustable process variables. It will be seen that the greater hardened depth of the plasma-treated alloy Ti – 6Al – 4V is further considerably increased in the alloy Ti – 6Al – 2Sn – 4Zr – 2Mo by deepening the diffusion layer.

The increased alloy content and the decreased amount of α-phase in the crystalline structure now makes it possible, with a core hardness of 400 HV, to obtain 0.05 and 0.1 hardnesses of 640 and 540 HV. The nitride hardness depth defined as the sum of the core hardness plus 50 HV units can be as high as 0.27 mm NHT.

The invention makes it possible, for the first time, to obtain in titanium alloys, hardened depths and hardness values which are comparable with the properties of nitrided steels. The process now described increases the depth of the diffusion layer, whose hardness increases continually, and this in turn increases its ability to support the outer, very hard layers.

This opens up the possibility of using the titanium alloys in highly stressed toothed driving wheels in the transmission systems of fixed wing and rotary wing aircraft, giving a weight saving of up to 40%. The increased hardened depth should also make it possible to make titanium alloy bearings. The use of connecting rods, piston rings, valve rockers and valves made of titanium alloys, which are about 40% less dense than steel, can reduce inertial forces and improve the efficiency of machines.

Machine parts such as conveying worms, cylinders, nozzles and sonotrodes made of titanium alloys and surface-hardened by a glow-discharge plasma treatment operate at improved efficiency in the processing of products which are subjected to corrosive and/or abrasive attack. The coating method proposed in the present invention should also increase the use of lightweight and/or rapidly moved parting tools made of titanium alloys.

Using treatment times of at least one hour, the upper limit being set only by economic considerations, hardened depths of 0.02 mm and more, preferably 0.25 mm, can be achieved. Products suitable for making from titanium alloys and treating in glow-discharge plasma include spindles, gearbox shafts, toothed wheels, toothed racks, rolls, pinions, synchronisation rings, plain, ball, roller and needle bearings, crankshafts and camshafts, connecting rods, piston rings, valve rockers, valves, the leading edges of steam turbine blades, conveying worms, cylinders, nozzles, sonotrodes and the cutting edges of parting tools.

CLAIMS

1. A technical titanium alloy forged, cast or sintered to form a machine part, the alloy having a tensile strength of at least 640 N/mm^2, the alloy containing between 3 and 28% of one or more of the elements aluminium, chromium iron, hafnium, cobalt, copper, manganese, molybdenum, nickel, niobium, palladium, silver, silicon, tantalum, vanadium, tungsten, tin, zirconium, beryllium, boron, carbon, oxygen, rare earths and yttrium, the remainder titanium together with unavoidable impurities, the surface layers of the alloy part being treated at over 700°C in glow-discharge plasma, in order to improve resistance to abrasion, including erosion and cavitation and/or in order to increase the permissible surface pressure, the treatment gas containing small quantities (partial pressures 0.1 to 500 mbar) of nitrogen.

2. A titanium alloy part as claimed in Claim 1, whose surface treatment includes the use of a gas which can contain, besides nitrogen, also small quantities of carbon and/or oxygen, for the purpose described in Claim 1.

3. A titanium alloy part as described in Claims 1 and 2, the treatment time being at least one hour and the hardened depth at least 0.02 mm, preferably 0.25 mm.

4. A titanium alloy as claimed in Claim 1, and in which the α-fraction, particularly in ($\alpha + \beta$)-alloys, is diminished by solution heat treatment.

5. A titanium alloy part as claimed in Claim 1, and in which the glow-discharge plasma treatment is conducted at a temperature which, in order to increase diffusion velocity, is not more than 200°C under the β-transition temperature for the alloy.

6. A titanium alloy part as claimed in Claim 1, and in which any internal stresses resulting from preliminary treatments, or any structural changes associated with volume changes, are largely nuetralised at the treatment temperature by low-stress annealing of the pre-worked parts, the temperature of the stress-relief annealing being of the same order, or if necessary up to 50°C higher, than the subsequent treatment temperature.

7. Use of a titanium alloy as claimed in Claim 1 for the purpose described in Claim 1, the machine parts being in a practically finished state before treatment by glow-discharge plasma, any subsequent machining, such as polishing, honing or lapping, for correcting small increases in volume or roughness, taking less than 0.020 mm of surface away.

8. Use of a technical titanium alloy as claimed in Claim 1 for the purpose described in Claim 1, for spindles, transmission shafts, toothed wheels, toothed rods, rolls, rollers, pinions, synchronisation rings, chain links, plain, ball, roller and needle bearings, crankshafts and camshafts, connecting rods, piston rings, valve rockers, valves, the leading edges of steam turbine blades, conveyor worms, cylinders, nozzles, sonotrodes and the cutting edges of parting tools.

9. Use of a titanium alloy for a machine part as claimed in Claim 1, the alloy being of the type: Ti–6Al–4V, and having the composition:
4.5 to 6.75% aluminium
3.5 to 4.5% vanadium
the remainder titanium and unavoidable impurities, for the purpose described in Claim 1.

10. Use of a titanium alloy for a machine part as claimed in Claim 1, the alloy being of the type: T1–6Al–2Sn–4Zr–2Mo–Si, and having the composition:
5.5 to 6.5% aluminium
3.6 to 4.4% zirconium
1.8 to 2.2% molybdenum
1.8 to 2.2% tin
at most 0.1% silicon
the remainder titanium and unavoidable impurities, for the purpose described in Claim 1.

11. Use of a titanium alloy for a machine part as claimed in Claim 1, the alloy being of the type: Ti–8Al–1Mo–1V, and having the composition:
7.35 to 8.35% aluminium
0.75 to 1.25% molybdenum
0.75 to 1.25% vanadium
the remainder titanium and unavoidable impurities, for the purpose described in Claim 1.

12. A machine part made from a titanium alloy and substantially as hereinbefore described.

Printed for Her Majesty's Stationery Office by Croydon Printing Company (UK) Ltd, 9/87, D8991685.
Published by The Patent Office, 25 Southampton Buildings, London WC2A 1AY, from which copies may be obtained.